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(21) International Application Number: PCT/US97/21698 (22) International Filing Date: 20 November 1997 (20.11.97) (30) Priority Data: 9624146.8 20 November 1996 (20.11.96) GB (71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): EIFFLER, Juergen [DE/DE]; Ystadweg 4, D-21682 Stade (DE). KARRASCH, Susanne [DE/DE]; Mittelweg 6a, D-21709 Himmelpforten (DE). (74) Agent: MORSE, Jonathan, W.; Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: POLYCARBONATES (57) Abstract <p>A polycarbonate containing one or more end-capping groups of formula (II) wherein A is an aliphatic hydrocarbon group or a group containing one or three aromatic or heteroaromatic rings to which the oxygens or carboxyl groups are directly linked, with the proviso that A does not contain a heteroatom outside the aromatic ring(s), n is 0 or 1, n' is 0 or 1, n'' is 0 or 1, provided that n' is 0 when n'' is 1, Y is a hydrocarbon group or a group of formula (VI) wherein E in each occurrence independently is O, R₂Si or R₂Si-O, R in each occurrence independently is H or C₁₋₆-alkyl, m in each occurrence independently is 0, 1, 2, 3, or 4, p is from 1 to 50 and q is 0 or 1.</p> <div style="text-align: center;"> $\begin{array}{c} \\ \text{O} \\ \\ [\text{C}(\text{O})]_n \\ \\ \text{A}-[\text{C}(\text{O})]_{n''}-\text{O}-[\text{C}(\text{O})]_{n'}\text{Y} \quad (\text{II}) \\ \\ [\text{C}(\text{O})]_{n''} \\ \\ \text{O} \\ \\ [\text{C}(\text{O})]_{n'}\text{Y} \end{array}$ </div> <div style="text-align: center;"> $\begin{array}{c} -(\text{CH}-)_m[\text{E}-(\text{CH}-)_m]_p-(\text{alkylene})_q-\text{H} \quad (\text{VI}) \\ \qquad \qquad \\ \text{R} \qquad \qquad \text{R} \end{array}$ </div>		

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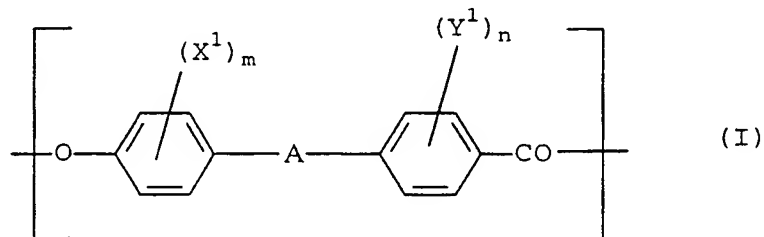
POLYCARBONATES

5 Polycarbonates are well known for their excellent properties. The glass transition temperature of polycarbonates is generally high. A high glass transition temperature is desired in many applications, for example when high temperature resistance is desired. Unfortunately, a high glass transition temperature renders the processing of the polycarbonate quite difficult. In certain applications, for example for producing hollow
10 articles or blow molded articles having thin walls, it would be highly desirable to provide a polycarbonate with a reduced glass transition temperature and, accordingly, improved melt flow properties at a given temperature.

European Patent Applications EP-A-0 565 311 and EP-A-0 508 775 suggest copolycarbonates which are said to have increased flow together with high thermal stability.
15 The copolycarbonate according to EP-A-0 565 311 is a block aromatic copolycarbonate which has from 2 to 30 mole percent, preferably from 5 to 20 mole percent, of the total repeating carbonate units derived from resorcinol. EP-A-0 508 775 suggests a method of producing copolymerized polycarbonates wherein the amount of optionally alkylated or halogenated resorcinol is 2 to 90 mole percent, based on the total amount of the aromatic
20 dihydroxy compounds. Preferably, the amount of the optionally alkylated or halogenated resorcinol is 5 to 70 mole percent, more preferably 10 to 60 mole percent. Unfortunately, resorcinol is considerably more sensitive to oxidation than bisphenol A. When such a high amount of resorcinol is used for the production of the polycarbonate, increased oxidation results in discoloration of the polymer solution and of the produced polycarbonate.

25 U.S. Patent No. 5,274,068 and European Patent Application EP-A-0 654 491 disclose a copolyester-carbonate with a reduced glass transition temperature T_g . The copolyester-carbonate according to U.S. Patent No. 5,274,068 are produced by reacting a dihydric phenol, a carbonate precursor and an aliphatic dicarboxylic acid having from 4 to 8 carbon atoms under certain conditions. The copolymers according to EP-A-0 654 491 are
30 based on bisphenol-A, an alkanedionic acid, and 1,1,1-tris-(4-hydroxyphenyl)ethane. The T_g is said to be reduced by the presence of aliphatic diester blocks. Unfortunately, large amounts of the aliphatic diacids are required to achieve a satisfactory reduction of the T_g . According to Examples 2 and 3 of EP-A-0 654 491 9 mole percent of the aliphatic diacid is used. Furthermore, the production process disclosed in U.S. Patent No. 5,274,068 requires
35 close control of the pH during the reaction.

Japanese Patent Application JP 06128371 A2 discloses a polycarbonate with good impact resistance and flowability. It contains repeating units of Formula I:



wherein A is $C[(CH_2)_jCH_3](CH_2)_kCH_3$, j is from 0 to 6, k is from 7 to 20, X^1 and Y^1 are

hydrogen, halogen, C_{1-8} -alkyl or C_{6-15} -aryl; and m and n are from 1 to 4. The

polycarbonate also contains repeating units of Formula I above wherein A is

C_{1-15} -alkylidene, C_{1-15} -alkylene, C_{6-15} -arylene, O, S, SO_2 , CO or a direct bond and X^1 ,

Y^1 , m and n are as defined above. The polycarbonate is preferably produced by reacting

Bisphenol-A, phosgene oligomer and 2,2-bis-(4-hydroxyphenyl)dodecane. Unfortunately,

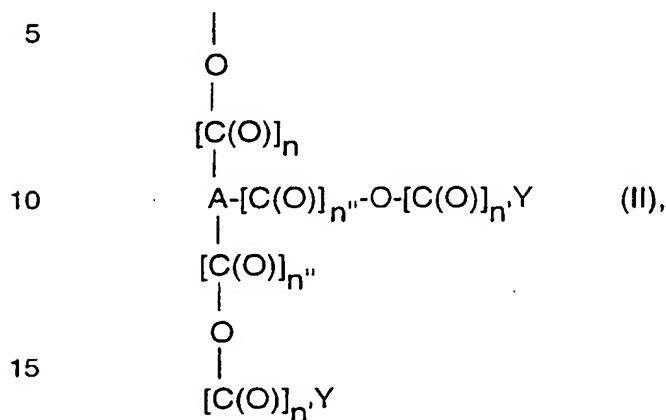
difficulties like low yields and production of by-products are experienced during the preparation of 2,2-bis-(4-hydroxyphenyl)dodecane.

European Patent Application 0 230 608 discloses a thermoplastic polyester-carbonate resin which contains copolymerized, in the polymer chain, divalent moieties of a monoester of trimellitic acid. The monoester of trimellitic acid is prepared by the reaction of trimellitic anhydride with an aliphatic alcohol. Unfortunately, high amounts of the above-mentioned divalent moieties have to be incorporated in the polyester-carbonate resin to achieve a substantive reduction of the glass transition temperature T_g . According to the Examples a T_g reduction between 1.4°C and 13.4°C is achieved when 10 or 20 mole percent of the above-mentioned divalent moieties, based on bisphenol A, are incorporated in the polyester-carbonate resin.

Another way of improving the melt flow properties of polycarbonates is the addition of a plasticizer to such resins. In Chemical Abstracts No. 121:110665, abstracting Japanese Patent Application JP 06116437 A2, bisphenol A terminated with ester groups, such as 2,2-bis-(4-acetyloxyphenyl)propane is suggested as a plasticizer for polycarbonates. Unfortunately, such plasticizers can migrate out of the polymer and are known to reduce the impact resistance of the polycarbonates. So far, the use of conventional plasticizers has not found commercial acceptance in polycarbonates.

One object of the present invention is to provide a new polycarbonate which has a reduced glass transition temperature and, accordingly, an improved flowability.

One aspect of the present invention is a polycarbonate which contains an end-capping group of Formula II:



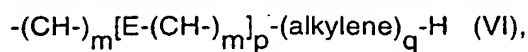
wherein

A is an aliphatic hydrocarbon group or a group containing one or three aromatic or heteroaromatic rings to which the oxygens or carboxyl groups are directly linked, with the proviso that A does not contain a heteroatom outside the aromatic ring(s),

n is 0 or 1,

n' is 0 or 1, n'' is 0 or 1, provided that n' is 0 when n'' is 1,

Y is a hydrocarbon group or a group of Formula



wherein

E in each occurrence independently is O, R₂Si or R₂Si-O,

R in each occurrence independently is H or C₁₋₆-alkyl,

m in each occurrence independently is 0, 1, 2, 3, or 4,

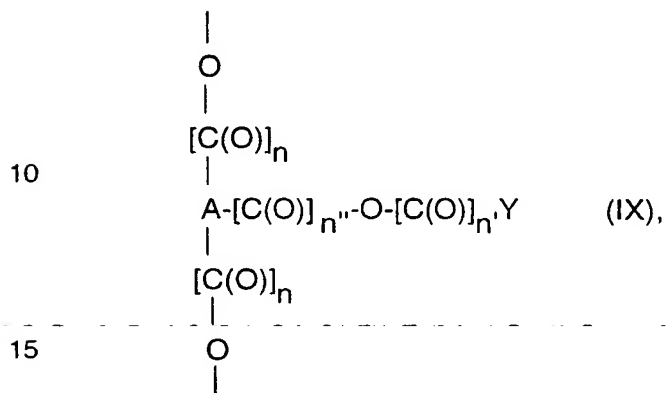
p is from 1 to 50 and

q is 0 or 1.

In the above Formula, n'' and n will generally be the same.

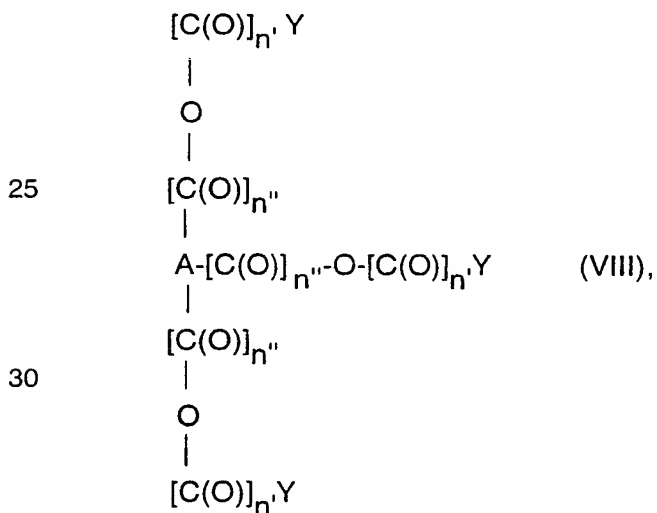
The term "polycarbonate" as used herein also includes carbonate copolymers, such as copolyester carbonates or copolyether carbonates.

A preferred aspect of the present invention is an above-mentioned polycarbonate which additionally contains one or more groups of Formula IX copolymerized
5 in the polymer backbone,



wherein A, Y, n, n' and n'' have the meanings indicated above.

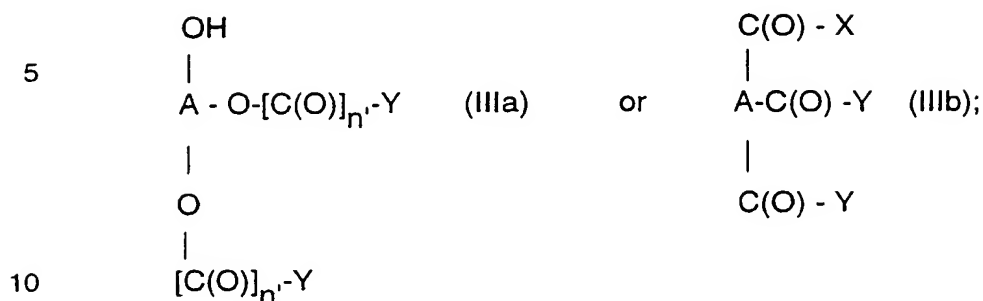
Another aspect of the present invention is a polycarbonate composition which
20 contains an above-mentioned polycarbonate and a compound of Formula VIII:



35 wherein A, Y, n and n' have the meanings indicated above.

Yet another aspect of the present invention is a process for producing a polycarbonate which comprises reacting at least

- (1) a carbonate precursor,
 (2) a dihydric phenol and
 (3) a compound of Formula IIIa or IIIb



wherein

X is halogen,
 n' is 0 or 1,

and A and Y have the meanings indicated above.

The polycarbonate of the present invention is useful for molding articles, particularly for producing blow molded articles, such as hollow articles having thin walls.

Accordingly, another aspect of the present invention is a molded article produced from the polycarbonate or polycarbonate composition of the present invention, particularly a molded article produced by blow-molding.

It has been found that the glass transition temperature of a polycarbonate can be lowered by incorporating one or more groups of Formula II above into the polycarbonate. Surprisingly, the polycarbonate or polycarbonate composition of the present invention has a reduced glass transition temperature, even if it contains a low level of a group of Formula II, for example from 0.5 to 5 mole percent.

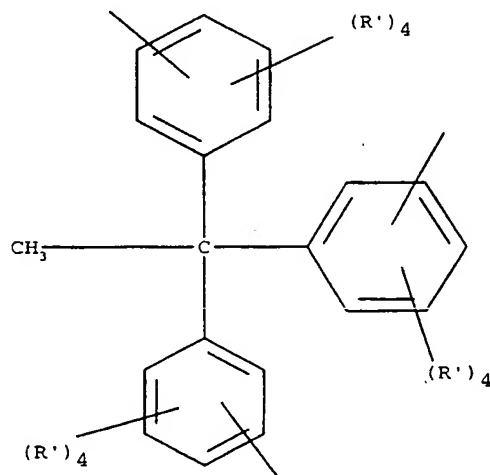
In Formula II, A can be an aliphatic hydrocarbon group which preferably contains from 1 to 5 carbon atoms, more preferably from 1 to 4 carbon atoms, most preferably from 1 to 3 carbon atoms. The hydrocarbon group is preferably saturated. Examples of preferred aliphatic hydrocarbon groups are methyl, ethyl, n-propyl or isopropyl.

However, in Formula II above A is preferably a group containing one or three aromatic or heteroaromatic rings to which the oxygens or carboxyl groups are directly linked,

with the proviso that A does not contain a heteroatom outside the aromatic ring(s). Preferred heteroatom(s) in the aromatic ring(s) are oxygen, sulfur or nitrogen. The aromatic ring(s) may be substituted with one or more alkyl or alkoxy groups which generally contain from 1 to 6, preferably from 1 to 3, more preferably 1 carbon atom(s). More preferred meanings for

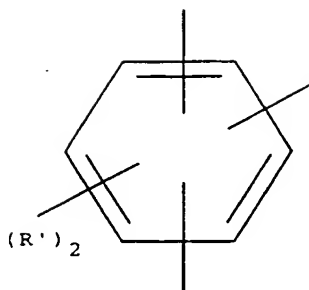
5 A are optionally alkylated or alkoxyated phenyl and (triphenyl)alkyl wherein the phenyl groups are optionally alkylated or alkoxyated. The alkyl group in (triphenyl)alkyl generally contains from 1 to 12, preferably from 1 to 6, more preferably from 1 to 3, most preferably 1 carbon atom(s).

- 10 In the case where n and n' are zero in Formula II, A is preferably (triphenyl)alkyl wherein the phenyl groups are optionally alkylated, as indicated above. The optionally alkylated phenyl groups can be bound to the same or different carbon atoms of the alkyl group. Preferably, they are bound to the same carbon atom. The most preferred meaning for A is



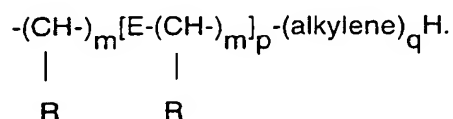
- 15 wherein R' in each occurrence independently is hydrogen, alkyl or alkoxy, more preferably hydrogen.

In the case where n and n' are 0 or preferably 1 in Formula II, A is preferably an optionally alkylated phenyl. The most preferred meaning for A is



wherein R' in each occurrence independently is hydrogen, alkyl or alkoxy.

- In Formula II, Y is a hydrocarbon group, such as aryl, aralkyl, alkaryl, alkenyl
 5 or, preferably, alkyl or a group of Formula



- 10 Among the listed meanings for Y the aliphatic, saturated groups are preferred.

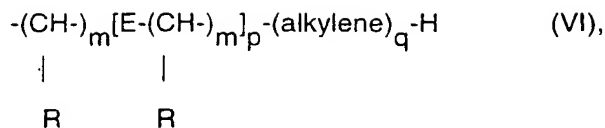
- The aryl, alkaryl or aralkyl group is optionally substituted at the aromatic ring with one or more inert substituents, for example halogen, such as chlorine, bromine or fluorine; or alkoxy or alkyl which generally contains from 1 to 6, preferably from 1 to 3 carbon atoms. Preferred aryl or alkaryl groups contain from 6 to 8 carbon atoms, such as phenyl,
 15 tolyl or xylyl. The aralkyl group preferably contains from 1 to 50, more preferably from 2 to 32, most preferably from 3 to 18 aliphatic carbon atoms.

The alkenyl group preferably contains from 2 to 50, more preferably from 2 to 32, most preferably from 3 to 18 aliphatic carbon atoms.

- The alkyl group generally contains from 1 to 50, preferably from 2 to 32, more
 20 preferably from 3 to 18 and most preferably from 4 to 18 aliphatic carbon atoms. Preferred alkyl groups are tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl or octadecyl.

Linear alkyl, alkenyl or alkylene groups are preferred.

Another preferred meaning for Y in Formula II is a group of formula



5 wherein

E in each occurrence independently is O, R₂Si or R₂Si-O,

R in each occurrence independently is H, or C₁₋₆ alkyl, preferably CH₃ or

C₂H₅,

10 the alkylene group, if present, generally contains from 1 to 50, preferably from 2 to 32, more preferably from 3 to 18 and most preferably from 5 to 18 aliphatic carbon atoms,

m in each occurrence independently is 0, 1, 2, 3, or 4, preferably from 1 to 3, more preferably 1 or 2,

p is from 1 to 50, preferably from 2 to 32, more preferably from 3 to 18 and

15 q is 0 or 1.

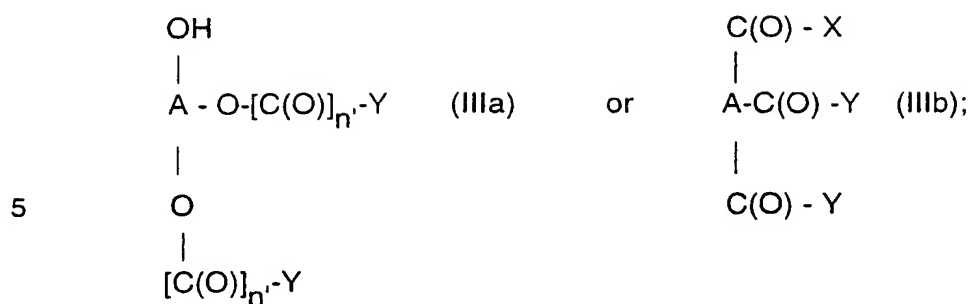
The polycarbonate contains an end-capping group of Formula II. This means that a polycarbonate can be capped at one or both ends of the polymer backbone with a group of Formula II. Furthermore, one or more side chains of a branched polycarbonate can be end-capped with a group of Formula II. It is to be understood that polycarbonates are
20 within the scope of the present invention even if only some of the polymer chains are end-capped with a group of Formula II.

The polycarbonate of the present invention is produced by reacting at least

(1) a carbonate precursor,

(2) a dihydric phenol, and

25 (3) a compound of Formula IIIa or IIIb as a comonomer



wherein

X is halogen, preferably chlorine or bromine,

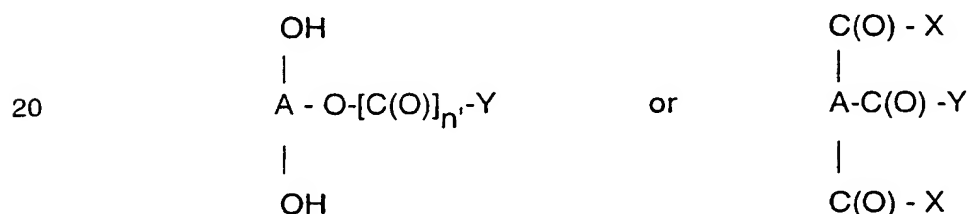
n' is 0 or 1, preferably 0, and

A and Y have the meanings indicated above.

The compounds of Formula IIIa are preferred over the compounds of Formula IIIb.

The molar ratio between the compound of Formula IIIa or IIIb and the dihydric phenol preferably is from 0.0001:1 to 0.25:1, more preferably from 0.001:1 to 0.1:1, most preferably from 0.005:1 to 0.05:1, particularly from 0.01:1 to 0.02:1.

The compound of Formula IIIa or IIIb can be used in combination with a corresponding divalent compound of formula



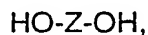
for producing a polycarbonate which additionally contains one or more of the above-mentioned groups of Formula IX copolymerized in the polymer backbone, that means one or more groups of Formula IX are located in the polymer chain. The molar ratio between the end-capping group(s) of Formula II and the divalent group(s) of Formula IX in the polycarbonate preferably is from 0.5 to 2:1, more preferably from 0.7 to 1.6:1. Combinations of groups of Formula II and of groups of Formula IX are particularly effective for lowering the glass transition temperature of the polycarbonate.

The compound of Formula IIIa or IIIb can also be used in combination with a known branching agent described further below. The molar ratio between the branching agent, if used, and the dihydric phenol preferably is from 0.0001:1 to 0.05:1, more preferably from 0.001:1 to 0.02:1. When using a combination of the branching agent and a compound of Formula IIIa or IIIb, generally from 1 to 99, preferably from 20 to 80 and most preferably from 45 to 55 percent of the compound of Formula IIIa or IIIb and from 99 to 1, preferably from 80 to 20 and most preferably from 55 to 45 percent of the branching agent can be used, based on the total weight of compound of Formula IIIa or IIIb and the branching agent.

The molar ratio between the compound of Formula IIIa or IIIb and the carbonate precursor preferably is from 0.0001:1 to 0.5:1, more preferably from 0.001:1 to 0.2:1, most preferably from 0.01:1 to 0.05:1. The molar ratio between the carbonate precursor and the dihydric phenol preferably is from 1:1 to 2:1, more preferably from 1:1 to 1.4:1, most preferably from 1:1 to 1.2:1.

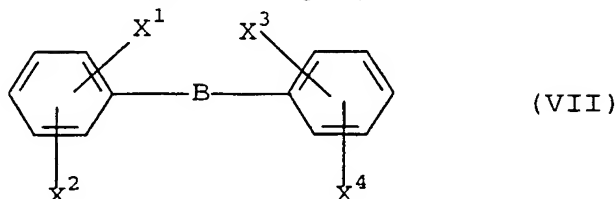
The carbonate precursor is for example a carbonyl halide, a diarylcarbonate or a bishaloformate. The carbonyl halides include carbonyl bromide, carbonyl chloride, and mixtures thereof. The bishaloformates include the bishaloformates of dihydric phenols such as bischloroformates of 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane or hydroquinone, or bishaloformates of glycols, such as bishaloformates of ethylene glycol. Carbonyl chloride, also known as phosgene, is preferred. Another preferred carbonate precursor is bis(trichloromethyl)carbonate, known as triphosgene.

The dihydric phenols employed in the practice of the present invention are dihydric phenols in which the sole reactive groups are the two phenolic hydroxyl groups. Useful dihydric phenols are for example those of the general Formula



wherein Z comprises a mononuclear or polynuclear aromatic group of 6 to 30 carbon atoms, to which the oxygen atoms are directly linked. The aromatic group may comprise one or more heteroatoms and may be substituted with one or more groups, for example one or more oxygens, nitrogens, sulfur, phosphorous and/or halogens, one or more monovalent hydrocarbon radicals, such as one or more alkyl, cycloalkyl or aryl groups; one or more alkoxy and/or aryloxy groups

Preferred meanings for Z are groups of Formula VII



wherein

B is a single bond, a divalent hydrocarbon radical containing 1 to 15 carbon atoms, preferably 1 to 6 carbon atoms, most preferably $-(CH_2)_2C-$, $-S-$, $-S-S-$, $-S(O)-$, $-S(O)_2-$, $-O-$ or $-C(O)-$ and

X^1 , X^2 , X^3 and X^4 independently are hydrogen; halogen, preferably chlorine, bromine or fluorine; a monovalent hydrocarbon radical, such as alkyl, cycloalkyl or aryl; alkoxy or aryloxy.

Preferred alkyl groups contain 1 to 6, more preferably 1 to 4 carbon atoms, such as methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl or tert-butyl or the pentyl or hexyl groups. Preferred cycloalkyl groups contain 5 or 6 carbon atoms, such as cyclopentyl or cyclohexyl. Preferred aryl and aryloxy groups contain 6 to 8 carbon atoms, such as phenyl, benzyl, phenoxy, tolyl or xylyl. Preferred alkoxy groups contain 1 to 6 carbon atoms, more preferably 1 to 4 carbon atoms, such as the methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, sec-butoxy or tert-butoxy groups.

Preferably, both phenolic hydroxyl groups in the dihydric phenol $HO-Z-OH$ are arranged in para-position to the radical B in the group of Formula I.

The dihydric phenols employed in the process of the present invention include the bis(aryl-hydroxy-phenyl)alkylidenes including their aromatically and aliphatically substituted derivatives, such as disclosed in U.S. Patent Nos. 2,999,835; 3,038,365; 3,334,154 and 4,299,928; and aromatic diols such as described in U.S. Patent No. 3,169,121.

Preferred examples of dihydric phenols of the general Formula $HO-Z-OH$ are bis(hydroxyphenyl)fluorenes, such as 9,9-bis-(4-hydroxyphenyl) fluorene; dihydroxy benzenes and the halo- and alkyl-substituted dihydroxy benzenes, such as hydroquinone, resorcinol, 1,4-dihydroxy-2-chlorobenzene, 1,4-dihydroxy-2-bromobenzene, 1,4-dihydroxy-2,3-dichlorobenzene, 1,4-dihydroxy-2-methylbenzene,

- 1,4-dihydroxy-2,3-dimethylbenzene and 1,4-dihydroxy-2-bromo-3-propylbenzene;
 alpha,alpha'-bis(hydroxyphenyl)-diisopropylbenzenes; dihydroxybiphenylenes, such as
 4,4'-dihydroxydiphenyl; the halo- and alkyl substituted dihydroxybiphenylenes, such as
 3,3'-dimethyl-4,4'-dihydroxydiphenyl, 3,3'-diethyl-4,4'-dihydroxydiphenyl,
 5 3,3'-dichloro-4,4'-dihydroxydiphenyl or 3,3',5,5'-tetrabromo-4,4'-dihydroxydiphenyl;
 bis(hydroxyphenyl)alkanes, such as bis(4-hydroxyphenyl)methane,
 1,1-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)propane, or, most preferably,
 2,2-bis(4-hydroxyphenyl)propane ("bisphenol A"), 1,1-bis(4-hydroxyphenyl)butane,
 4,4-bis(4-hydroxyphenyl)heptane, alkyl-, aryl- or halo-substituted bis(hydroxyphenyl)alkanes,
 10 such as 1,1-bis(4-hydroxyphenyl)-1,1-diphenyl methane,
 1,1-bis(3-methyl-4-hydroxyphenyl)ethane, 1-phenyl-1,1-bis(4-hydroxyphenyl)ethane
 ("bisphenol-AP"), 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane,
 1-phenyl-2,2-bis(4-hydroxyphenyl)propane ("phenyl substituted bisphenol A"),
 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane ("tetrabromo bisphenol-A"),
 15 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane ("tetrachloro bisphenol-A"),
 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane ("tetramethyl bisphenol-A");
 2,2-bis(3,5-difluoro-4-hydroxyphenyl)butane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl)pentane,
 3,3-bis(3-methyl-4-hydroxyphenyl)hexane, 2,2-bis(3-ethyl-4-hydroxyphenyl)octane,
 2,2-bis(3,5-dibromo-4-hydroxyphenyl)nonane,
 20 2,2-bis(3,5-isopropyl-4-hydroxyphenyl)nonane, or 2,2-bis(3-propyl-4-hydroxyphenyl)decane;
 optionally alkyl-, aryl- or halo-substituted bis(hydroxyphenyl)cycloalkanes, such as
 1,1-bis(4-hydroxyphenyl)cyclopentane, 1,1-bis(4-hydroxyphenyl)cyclohexane,
 1,1-bis(4-hydroxyphenyl)cycloheptane, 1,1-bis(4-hydroxyphenyl)cyclooctane;
 1,1-bis(4-hydroxyphenyl)cyclodecane or
 25 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane; optionally alkyl-, aryl- or halo-
 substituted bis(hydroxyphenyl)ethers, such as bis(3-chloro-5-methyl-4-hydroxyphenyl)ether,
 bis(3,5-dibromo-4-hydroxyphenyl)ether, bis(3,5-dichloro-4-hydroxyphenyl)ether,
 bis(3-ethyl-4-hydroxyphenyl)ether, bis(3-methyl-4-hydroxyphenyl)ether or
 bis(4-hydroxyphenyl)ether; bis(hydroxyaryl)ketones, bis(4-hydroxyphenyl)ketone; optionally
 30 alkyl-, aryl- or halo-substituted bis(hydroxyaryl)sulfones, preferably
 bis(hydroxyphenyl)sulfones, such as bis(3,5-dimethyl-4-hydroxyphenyl)sulfone,
 bis(3,5-diisopropyl-4-hydroxyphenyl)sulfone, bis(3-methyl-5-ethyl-4-hydroxyphenyl)sulfone,
 bis(3,5-dibromo-4-hydroxyphenyl)sulfone, bis(3-chloro-4-hydroxyphenyl)sulfone,
 bis(3-methyl-4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfone,
 35 bis(3-hydroxyphenyl)sulfone, or bis(2-hydroxyphenyl)sulfone; bis(hydroxyphenyl)sulfoxides,

such as bis(3,5-diisopropyl-4-hydroxyphenyl)sulfoxide, bis(3,5-dibromo-4-hydroxyphenyl)sulfoxide, bis(3,5-dimethyl-4-hydroxyphenyl)sulfoxide, bis(3-methyl-5-ethyl-4-hydroxyphenyl)sulfoxide, bis(3-methyl-4-hydroxyphenyl)sulfoxide or bis(4-hydroxyphenyl)sulfoxide. The most preferred dihydric phenol is bisphenol A.

5 Other examples of suitable dihydric phenols are listed in U.S. Patent No. 4,627,949, column 2, line 68 to column 3, lines 1-22, in U.S. Patent No. 4,962,144, column 2, lines 17-46 and in European Patent Application EP-A-0 423 562, page 2, lines 24-55 and page 3, lines 1-19. Mixtures of two or more dihydric phenols may also be used, for example a mixture comprising 3 to 97 percent of bisphenol A and 97 to 3 weight
10 percent of another dihydric phenol, such as 9,9-bis-(4-hydroxyphenyl)fluorene.

The production of a compound of Formula IIIa or IIIb can be carried out before or during the compound of Formula IIIa or IIIb is reacted with a carbonate precursor and a dihydric phenol to produce the polycarbonate of the present invention. The compound of Formula IIIa or IIIb can be isolated and optionally purified before it is reacted with a
15 carbonate precursor and a dihydric phenol. However, the compound of Formula IIIa or IIIb is preferably produced *in situ* during the process of the present invention for producing a polycarbonate.

The compounds of Formula IIIa can be produced by reacting a compound of Formula IVa



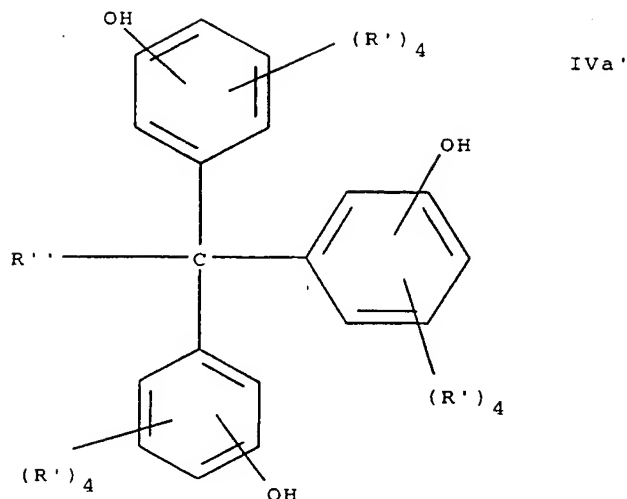
25 with a compound of Formula Va



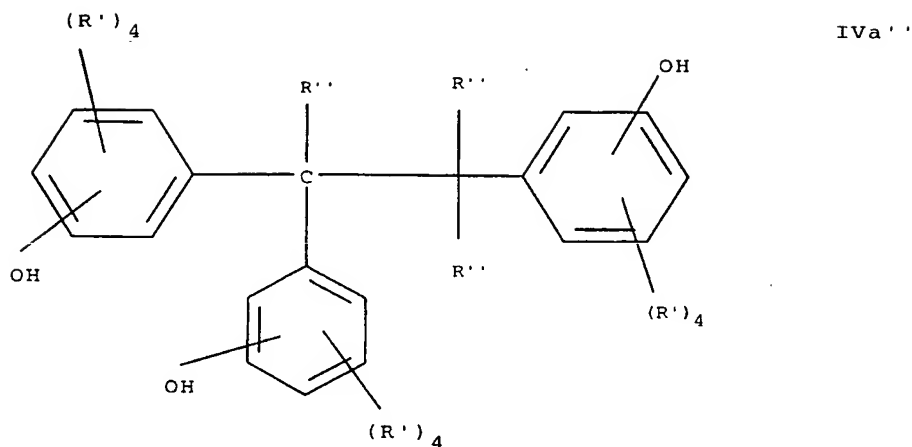
wherein A and Y have the meanings indicated above and

X' is halogen, -C(O)-halogen, -C(O)OH or epoxy.

Preferred compounds of Formula IVa are optionally alkylated or alkoxyated
30 trisphenols. Preferred trisphenols are compounds of Formulas IVa' and IVa''



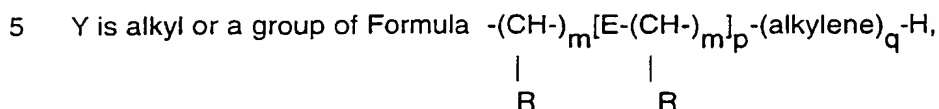
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- The compounds of Formula IVa' are the most preferred ones. In Formulas
- 10 IVa' and IVa'', R' in each occurrence independently is hydrogen, alkyl or alkoxy which generally contains from 1 to 6, preferably from 1 to 3, more preferably 1 carbon atom(s). Most preferably, R' in each occurrence is hydrogen. R'' in each occurrence independently is hydrogen, alkyl or alkoxy which generally contains from 1 to 12, preferably from 1 to 6, more preferably from 1 to 3, and most preferably 1 carbon atom(s). The phenolic hydroxyl groups
- 15 are preferably arranged in the para-position.

Other preferred trisphenols of Formula IVa are the trihydroxybenzenes, such as 1,2,4-trihydroxybenzene and particularly 1,3,5-trihydroxybenzene.

Preferred compounds of Formula Va, that means a compounds of Formula X'-Y are those wherein



R is H or CH₃, E is O, R₂Si or R₂Si-O, m is 0, 1 or 2, p is from 1 to 50, q is 0 or 1 and

X' is halogen, -C(O)-halogen, -C(O)OH or epoxy. Mixtures of compounds of Formula Va can
10 also be reacted with a compound of Formula IVa.

The most preferred compounds of Formula X'-Y are those wherein X' is halogen or -C(O)-halogen, whereby halogen preferably means bromine or more preferably chlorine. Most preferably, Y means a linear alkyl group which contains from 1 to 50, preferably from 2 to 32, more preferably from 3 to 18 aliphatic carbon atoms. Most
15 preferably a mixture of compounds of Formula X'-Y is used wherein Y means alkyl groups containing 6, 8 and 10 aliphatic carbon atoms.

The molar ratio between the compound of Formula IVa and the compound of Formula X'-Y is preferably from 0.1 to 10:1, more preferably from 0.5 to 5:1 more from preferably 1:1 to 2.5 :1, most preferably greater than 1.25:1 to 2.5:1.

20 The reaction can be carried out in a single-phase or a two-phase system. When the reaction is carried out in a single-phase system, usually an inert organic diluent is chosen wherein the compounds of Formula IVa and of Formula X'-Y are soluble. Useful solvents depend on the specific starting materials used for the reaction and are known to the skilled artisan. Exemplary of useful solvents are halogenated solvents, for example,
25 chlorinated hydrocarbons, such as o-, m-, or p-chlorobenzene or methylene chloride, or hydrocarbons, such as pentane, cyclopentane or mixtures thereof, hexane, acyclic or cyclic ethers, such as dioxane or tetrahydrofuran or ketones, such as acetone. Preferably the reaction mixture is substantially free of water, in order to avoid hydrolysis of the compound of Formula X'-Y as a side reaction. Dimethyl formamide, methanol or ethanol are useful if X'
30 in the Formula X'-Y is halogen.

When using a two-phase system, the compound of Formula X'-Y can be dissolved in an organic solvent, such as methylene chloride or monochlorobenzene.

5 The compound of Formula IVa can be dissolved in diluent which is not fully miscible with the above-mentioned organic solvent. Exemplary of such diluents are an aqueous basic liquid, such as aqueous sodium hydroxide, potassium hydroxide or dilute aqueous ammonia. Alternatively, the compound of Formula IVa can be treated with solid Na_2CO_3 or K_2CO_3 in an acetone dispersion.

10 Generally the reaction is carried out at an elevated temperature, preferably at a temperature of from 25°C to 120°C , more preferably from 40°C to 100°C . The pressure preferably is from 0.1 to 5 bar, more preferably from 0.5 to 2 bar, most preferably about 1 bar. Preferably the reaction is carried out in the presence of a basic compound, such as an alkali metal or alkaline earth metal hydroxide or carbonate, preferably sodium hydroxide or sodium carbonate, or an
15 organic amine, such as trimethyl amine or triethyl amine. The molar ratio between the base and the compound of Formula X'-Y is preferably from 0.8 to 3:1, more preferably about 1:1. The reaction is generally completed within 2 to 15 hours, in many cases within 2 and 4 hours. Depending on the starting materials used for the reaction, an inorganic salt may be produced as a by-product which usually
20 precipitates from the reaction mixture. It is preferably removed from the reaction mixture in a known manner, such as filtration.

The produced reaction mixture can be reacted with a carbonate precursor and a dihydric phenol as described further below. Prior to this reaction it is optionally subjected to one or more purification steps, such as the above-mentioned
25 filtration, phase separation in the case of a two-phase reaction mixture or separation of non-reacted starting materials. The separation of non-reacted starting materials can, for example, be carried out by adding a solvent in which the compound of Formula IVa is not soluble and recycling the precipitated compound of Formula IVa.

30 If the molar ratio between the compound of Formula IVa and the compound of Formula X'-Y generally is from 0.7 to 1.5:1, preferably from greater

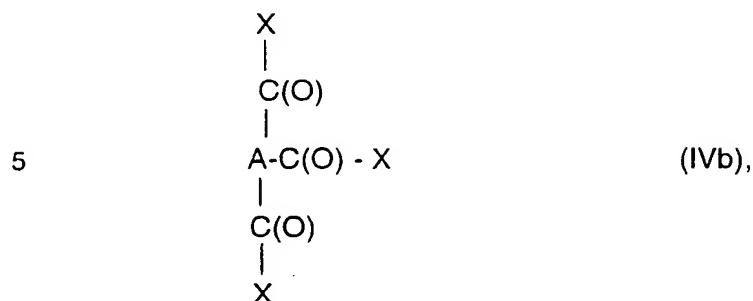
than 0.8 to 1.2:1, major amounts of a mono-substituted compound of the Formula $(\text{HO})_2\text{A} - \text{O} - [\text{C}(\text{O})]_{n'} - \text{Y}$ are prepared in addition to the disubstituted compound of Formula IIIa. Such mono-substituted compounds are particularly suitable for being incorporated into the polycarbonate backbone.

5 If the molar ratio between the compound of Formula IVa and the compound of Formula X'-Y generally is from 0.2 to 1:1, preferably from 0.4 to less than 0.8:1, predominantly a disubstituted compound of Formula IIIa is prepared. Such compounds are particularly suitable for end-capping the polycarbonate.

10 If the molar ratio between the compound of Formula IVa and the compound of Formula X'-Y is further decreased, for example, from 0.01 to 0.33:1, preferably from 0.05 to 0.1:1, increasing amounts of a tri-substituted compound of Formula VIII shown above (wherein n'' is 0) are produced which can be mixed with a polycarbonate to decrease its glass transition temperature.

15 The reaction product between the compound of Formula IVa and the compound of Formula X'-Y usually contains mono-, di- and tri-substituted compounds. Additionally, the reaction product generally contains unreacted compound of Formula IVa. These compounds can be separated from each other by known techniques, for example, by filtration, distillation or crystallization. However, it is generally not necessary to subject the reaction product to a separation step before
20 it is reacted with a polycarbonate precursor and a dihydric phenol. Depending on the molar ratio between the compound of Formula IVa and the compound of Formula X'-Y, the amount of unreacted compound of Formula IVa generally is from 0.1 to 50 mole percent, typically from 2 to 45 mole percent, based on the total amount of the reaction product. The non-reacted compound of Formula IVa can be used together
25 with the compound of Formula IIIa in the reaction with a carbonate precursor and a dihydric phenol.

 The compounds of Formula IIIb can be produced by reacting a compound of Formula IVb



with a compound of Formula HO-Y,

wherein X is halogen, preferably chlorine, and

A and Y have the meanings indicated above.

15 Preferred compounds of Formula IVb are those wherein A is a benzene ring which is optionally substituted with one or two alkyl or alkoxy groups, more preferably an unsubstituted benzene ring.

Preferred compounds of Formula HO-Y are those wherein Y is alkyl or a group of Formula $-(CH-)_m[E-(CH-)_m]_p-(alkylene)_q-H$,



R is H or CH₃, E is O, m is 0, 1 or 2, q is 0 or 1 and p is from 1 to 50, preferably from 2 to 32, more preferably from 3 to 18. Most preferably a mixture of compounds of Formula HO-Y is used wherein Y means alkyl groups containing 6, 8 and 10 aliphatic carbon atoms.

25 The molar ratio between the compound of Formula IVb and the compound HO-Y is preferably from 0.1 to 10:1, more preferably from 0.5 to 5:1 more from preferably 1:1 to 2.5:1, most preferably greater than 1.25:1 to 2.5:1.

The reaction can be carried out in a single-phase or a two-phase system.

30 Exemplary of useful solvents are the same as those listed above for the reaction between the compounds of Formula IVa and the compound of Formula X'-Y. The reaction conditions, such as temperature, pressure, molar ratios, presence of a basic compound, purification step(s) and product distributions are substantially the same as those described above for the reaction between the compound of Formula IVa and the compound of Formula X'-Y.

35 Alternatively, a compound of Formula IIIa or a compound of Formula VIII can be produced by reacting cyanuric chloride with a compound of Formula HO-Y.

The compounds of Formulas IIIa and IIIb are useful in a process for producing a polycarbonate which comprises reacting at least

(1) a carbonate precursor,

(2) a dihydric phenol and

5 (3) a compound of Formula IIIa or IIIb which is produced prior to the polycarbonate production or *in situ* during the polycarbonate production.

As indicated above, the compound of Formula IIIa or IIIb can be used in combination with a branching agent. Suitable branching agents are, for example, described in U.S. Patent Nos. 3,544,514 and 4,680,370 and the published European Patent Application
10 EP-A-0 423 562, page 3, line 43 to page 4, line 2. Useful branching agents have three or more functional groups, preferably three or more phenolic hydroxyl groups. Preferred branching agents are 1,3,5-tris(4-hydroxyphenyl)benzene, 1,1,1-tris(4-hydroxyphenyl)ethane, tris(4-hydroxyphenyl)-phenylmethane or 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)propane. Other preferred branching agents are
15 tri(p-hydroxyphenyl)phosphines, tri-(p-hydroxyphenyl)phosphine oxides, tri-(p-hydroxyphenyl)phosphites, tri-(p-hydroxyphenyl)phosphates, as described in U.S. Patent No. 4,680,370, 2,4-dihydroxy-benzoic acid, cyanuric chloride, trimellitic or trimesic acid or acid chlorides or 3,3-bis-(4-hydroxy-3-methyl-phenyl)2-oxo-2,3-dihydroindol. The last
20 mentioned compound is useful as a branching agent, although it does not contain three phenolic hydroxyl groups but an amide group in addition to two phenolic hydroxyl groups.

In addition to compounds (1), (2) and (3) and the optional branching agent described above, a monohydric phenol can be used for the preparation of the polycarbonate of the present invention.

The molar ratio between the dihydric phenol and the monohydric phenol
25 preferably is on the average at least 1:1, more preferably at least 5:1, most preferably at least 10:1. The molar ratio between the dihydric phenol and the monohydric phenol preferably is on the average up to 1000:1, more preferably up to 100:1, most preferably up to 50:1. A particularly preferred amount of the monohydric phenol is from 0.01 to 5 percent, based on the weight of the dihydric phenol. The monohydric phenol may be used as a chain
30 stopper or for controlling the molecular weight of the product. Suitable monohydric phenols are for example phenol, lower alkyl phenols, such as 4-methylphenol, 3-ethylphenol,

5-propylphenol, 4-isopropylphenol, 5-butylphenol, 3-isobutylphenol, 4-tertiary butylphenol, octyl phenol or 4-pentylphenol; aryl phenols, such as 4-phenyl phenol or 5-phenyl phenol; cycloaliphatic phenols, such as 4-cyclohexyl phenol or 3-cyclohexylphenol; or monophenol alkanes, such as 2,2-(4-hydroxyphenyl-4-methoxyphenyl) propane or 3-hydroxyphenyl ethane. The most preferred monohydric phenol is tertiary butylphenol, most preferably 4-tertiary butylphenol. Other preferred chain stoppers and their useful amounts are disclosed in European patent application EP-A-0 423 562, page 4, lines 5 to 21.

If the preparation of a copolyester or copolyether carbonate is desired, additionally a dicarboxylic acid or dicarboxylic acid halide or a diol can be reacted with the above-described carbonate precursor, dihydric phenol and compound of Formula IIIa or IIIb.

Useful aromatic dicarboxylic acids or dicarboxylic acid dihalides are, for example, terephthaloyl dichloride or isophthaloyl dichloride. If an aromatic dicarboxylic acid or dicarboxylic acid dihalide is used for the preparation of a copolyester carbonate, it is preferably used in an amount of from 0.1 to 50 mole percent, more preferably from 1 to 30 mole percent, based on the molar amount of the dihydric phenol.

Useful aliphatic dicarboxylic acids or dicarboxylic acid dihalide preferably contain from 4 to 12 carbon atoms, such as adipic acid, decanoic acid, undecanoic acid or dodecanoic acid. Useful diols are preferably dihydric phenols, such as resorcinol. If a diol or an aliphatic dicarboxylic acid (dihalide) is used for the preparation of a copolyether carbonate, it is preferably used in an amount of from 0.1 to 20 mole percent, more preferably from 2 to 10 mole percent, based on the molar amount of the dihydric phenol.

The polymerization process can be carried out by standard techniques well known in the art. Depending on the type of reaction diluent, the reaction can be conducted a) as a two-phase process or b) in a homogeneous solution.

For conducting a two-phase reaction, the reaction diluent comprises an aqueous and an organic phase. The volume ratio between the aqueous phase and the organic phase preferably is from 1:2 to 2:1, more preferably from 1:1.5 to 1.5:1, most preferably 1:1. The interphase preferably is from 0.1 m²/l to 50 m²/l. The reaction diluents are preferably water and one or more water-immiscible solvents, preferably one or more chlorinated solvents. Preferred chlorinated solvents are chlorobenzene, dichlorobenzene, ethylene chloride or, most preferably, methylene chloride. The most useful bases are alkali hydroxides or alkaline earth hydroxides, such as NaOH, KOH,

CsOH, $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$ or the corresponding oxides which form hydroxides in contact with water, such as CaO. The two-phase process is particularly suitable if phosgene is used in the reaction.

The use of a catalyst may be advantageous, particularly if phosgene is used in the reaction. Such catalysts are, for example, tertiary or quaternary organic bases, such as trimethyl amine, triethyl amine, dimethyl aniline, diethyl aniline, dimethylcyclohexylamine or pyridine; or the corresponding hydrohalides, such as triethyloctadecyl ammonium chloride, trimethylbenzylammonium fluoride, triethylbenzylammonium chloride, dimethyldodecyl ammonium chloride, dimethylbenzyl phenyl ammonium chloride, trimethylcyclohexyl ammonium bromide or N-methylpyridonium chloride; or tetramethylammonium hydroxide.

For conducting the reaction in a homogeneous solution, generally one or more organic solvents are used which are inert towards the reactants and which are preferably polar. Preferred organic solvents are chlorinated solvents, such as chlorobenzene, dichlorobenzene, ethylene chloride or, most preferably, methylene chloride; ethers, such as dimethyl ether, tetrahydrofuran, dimethoxyethane or, most preferably, dioxane; formamides, such as dimethylformamide or dimethylacetamide; esters, such as acetic ester; or ketones, such as acetone. Most preferably, chlorinated solvents and/or ethers are used. Preferred bases are amines, more preferably tertiary aliphatic amines, such as trimethyl amine or triethyl amine, or aromatic amines, such as pyridine.

The reaction temperature preferably is from 20°C to 100°C, more preferably from 20°C to 70°C, most preferably from 25°C to 50°C, depending on the reaction diluent. The reaction is preferably conducted at about ambient pressure.

Preferably a compound of Formula IIIa or IIIb is dissolved in an aqueous reaction diluent, such as aqueous sodium hydroxide, or more preferably in an organic reaction diluent, such as methylene chloride. The order of contacting the compound of Formula IIIa or IIIb, the dihydric phenol and the carbonate precursor is not very critical. However, the compounds of Formula IIIa or IIIb is preferably added to the dihydric phenol before the dihydric phenol is contacted with the carbonate precursor.

The compounds of Formula IIIa, preferably those wherein n' is 0, can also be used in a melt transesterification process for producing polycarbonates of a decreased T_g . Melt transesterification processes are generally described by D. Freitag et al., Aromatic Polycarbonates, in "Encyclopedia of Polymer Science and Engineering", volume 11, pages 651-652, 1982, A Wiley-Interscience publication.

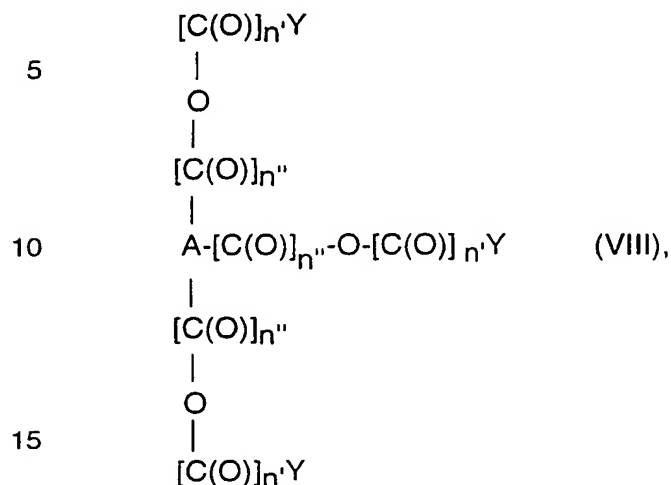
The produced polycarbonates preferably have a number average molecular weight of from 10,000 to 250,000, more preferably from 12,000 to 120,000 and most preferably from 15,000 to 60,000.

The polymer or polymer composition of the present invention can be blended with optional additives, such as an inorganic and/or organic light diffuser, a UV stabilizer, such as a benzotriazole or a benzophenone, a heat stabilizer, such as a phosphine, phosphite or diphosphonite, optionally in combination with a hindered phenol, a dye or an optical brightener. Such additives are known in the art.

The polycarbonate or polycarbonate composition of the present invention is useful for producing a molded article, preferably articles of thin walls. By "thin walls" generally walls of from 0.2 to 3 mm, preferably from 0.3 to 2 mm, more preferably from 0.5 to 1.5 mm are meant. It is particularly suitable for blow-molding applications. Processes for molding polycarbonates are known in the art. Preferred extrusion and injection molding temperatures are from 200°C to 360°C, more preferably from 220°C to 340°C, most preferably from 240°C to 300°C.

It has been surprisingly found that the glass transition temperature of a polycarbonate containing one or more groups of Formula II is significantly reduced, even if only from 0.1 to 10 percent, typically from 0.5 to 5 percent of a compound of Formula IIIa or IIIb is incorporated into the polycarbonate, based on the molar amount of a dihydric phenol that is incorporated into the polycarbonate. It has been found that the glass transition temperature of such a polycarbonate is generally at least 5°C lower, usually at least 10°C lower, in many cases at least 20°C lower and in some cases even at least 30°C lower than the glass transition temperature of a corresponding polycarbonate of essentially the same composition and molecular weight except that it does not contain groups of Formula II.

The glass transition temperature of a polycarbonate can be further reduced by blending the polycarbonate of the present invention with a compound of Formula VIII



wherein A, Y, n, n' and n'' have the meanings indicated above.

The resulting polycarbonate composition preferably contains from 0.1 to 10 percent, more preferably from 0.5 to 5 percent, most preferably from 1 to 2 percent of one or more compounds of Formula VIII, based on the weight of the polycarbonate. The compound of Formula VIII acts as a plasticizer in the polycarbonate.

The invention is further illustrated by the following examples which should not be construed to limit the scope of the present invention. Unless stated otherwise all parts and percentages are given by weight.

Examples

Molecular weights are determined by GPC (gel permeation chromatography).

The glass transition temperature T_g is determined by Differential Scanning Calorimetry.

Example 1I. Reaction of trimellitic trichloride (TMTC) with dodecanol (molar ratio of 1:1):

0.106 g (0.4 mmole) of TMTC were dissolved in 20 mL of methylene chloride in a 50 mL glass reactor. 0.0745 g (0.4 mmole) of dodecanol were added. Then, 0.4 mL of 1 n NaOH and 1 mL of water were added. The solution was stirred for half an hour at room temperature and then heated to refluxed for an additional 3 hours.

II. Condensation of the reaction product of trimellitic trichloride and dodecanol with bisphenol A and phosgene:

4.56 g (20 mmole) of bisphenol A are added into a 100 mL glass reactor which had been purged with nitrogen. Then the bisphenol A was dissolved in 23 mL of 1.5 n NaOH. The solution was stirred and heated to 35°C until the bisphenol A had been completely dissolved. The reaction product of TMTC with dodecanol in 20 mL of methylene chloride was added at once and the solution was vigorously stirred. The molar ratio of comonomer prepared from TMTC and dodecanol to bisphenol was 0.02:1. 12 mL of a solution of triphosgene (bis(trichloromethyl)carbonate) in methylene chloride (3.0 g in 30 mL) were added at a rate of 0.05 mL/10 seconds. Then 4 mL of a solution of 0.425 g of p-tert-butylphenol in 25 mL of methylene chloride were added at once. The molar ratio of bisphenol A to p-tert-butylphenol was 44. Another 12 mL of the same triphosgene solution was added at the same rate. The pH was kept between 9 and 10.5 by the addition of 2 mL of 1.5 n NaOH. After all of the triphosgene solution had been consumed, 2 mL of a solution of 2.5 g of triethylamine in 10 mL of methylene chloride were added together with 2 mL of 30 weight percent aqueous NaOH (pH of 11.9). The solution was allowed to stir for 10 minutes. The phases were separated and the organic phase was washed at first with 75 mL of 2 n HCl and then 3 times with distilled water until its pH was neutral. The organic phase was dried over Na_2SO_4 and methylene chloride was evaporated. A clear, transparent, flexible film was obtained which was dried under vacuum at 70°C overnight. Yield: 3.8 g. IR and NMR spectroscopies confirm that the reaction product of trimellitic trichloride and dodecanol was incorporated as a comonomer in the polycarbonate.

M_n (g/mole) : 13100; M_w (g/mole) : 50800.

The glass transition temperature T_g was 138°C. For comparison, a polycarbonate was prepared from bisphenol A and phosgene in the same manner, except that no reaction product of trimellitic trichloride and dodecanol was used as a comonomer. The T_g was about 148°C.

- 5 The example showed that the incorporation of a comonomer prepared from TMTC and dodecanol significantly reduced the T_g even if the molar ratio of the comonomer to bisphenol A was only 0.02:1.

Example 2

I. Reaction of TMTC with polyoxyethylene (4)-laurylether (Brij 30, Aldrich):

- 10 0.106 g (0.4 mmole) of TMTC are dissolved in 20 mL of methylene chloride. Then 0.145 g of Brij 30 were dissolved in this solution. 0.4 mL of 1.5 n NaOH were added and the solution was kept under reflux for 2 hours.

II. The interfacial polycondensation of the reaction product with bisphenol A and phosgene and its purification and isolation was carried out as described in Example

- 15 1. The molar ratio of the reaction product to bisphenol was 0.02:1.

M_n : 13,200; M_w 55700. The glass transition temperature is 132°C.

Comparative Example A

I. Polycondensation of non-modified (non-alkylated) TMTC with bisphenol A and phosgene at a molar ratio of TMTC to bisphenol A of 0.02:1:

- 20 II. 0.106 g of TMTC was dissolved in a solution of 4.56 g bisphenol A in 23 mL of 1.5 n NaOH. The interfacial polycondensation was carried out as described in Example 1. An insoluble jelly, crosslinked polycarbonate was obtained.

- Comparison of Comparative Example A with Examples 1 and 2 showed that a transparent polycarbonate having a reduced T_g was only obtained if the trifunctional
25 monomer TMTC had been reacted with an alcohol HO-Y according to the invention.

Example 3I. Reaction of a trisphenol with octyl bromide in methanol (molar ratio of 1:1):

0.1224 g of tris(4-hydroxyphenyl) ethane (THPE) was dissolved in 30 mL of methanol. 0.4 mL of a 1 n NaOH solution was added and the reaction mixture was heated to 50°C. 0.077 g of octyl bromide dissolved in 20 mL of methanol was added within 30 minutes to the THPE solution. The reaction temperature was kept at 50°C for 3.5 hours. The methanol was then completely evaporated at 45°C in a vacuum of lower than 10 mbar.

II. Polycondensation of the reaction product with bisphenol A and phosgene at a molar ratio of reaction product to bisphenol A of 0.02:1.

The dry reaction residue was dissolved together with 4.56 g of bisphenol A in 30 mL of 1.5 n NaOH at a temperature of 35°C. 13.4 mL of methylene chloride were added and the phosgenation, reaction with triethylamine and aqueous NaOH, purification and isolation of the polymer was carried out as described in Example 1. A clear, transparent polycarbonate film of 3.78 g weight was obtained.

M_n : 13600; M_w : 34700. The glass transition temperature was 129°C.

Comparative Example B

I. Polycondensation of THPE with bisphenol A and phosgene (molar ratio of THPE to bisphenol A of 0.02:1):

0.1224 g of THPE were dissolved together with 4.56 g of bisphenol A in 30 mL of 1.5 n NaOH. The molar ratio of THPE to bisphenol A was 0.02:1. The interfacial polycondensation was carried out as described in Example 1. A crosslinked, jelly product was obtained which was not soluble in methylene chloride any more.

Comparison of Comparative Example B with Example 3 showed that a soluble, transparent polycarbonate having a reduced glass transition temperature was only obtained if the trisphenol had been reacted with a compound of Formula X"-Y, such as octyl bromide.

Example 4

- I. Reaction of 1,3,5-trishydroxybenzene (phloroglucindihydrate) with octane mono-acid chloride (molar ratio of 1:1).

5 0.162 g (1 mmole) of phloroglucindihydrate was dissolved in a mixture of 1 mL of NaOH and 5 mL of water at 50°C. 10 mL of methylene chloride were additionally brought into the reactor. A solution of 0.162 g (1 mmole) of octane mono-acid chloride dissolved in 5 mL of methylene chloride was slowly dropped into this solution and reacted under reflux. The reaction mixture was kept at 60°C for another 3 hours.

- 10 II. Polycondensation of the reaction product with bisphenol A and phosgene (molar ratio of the reaction product to phosgene of 0.05:1):

The reaction mixture was brought into a solution of 4.56 g of bisphenol A dissolved in 23 mL of 1.5 n NaOH. The polycondensation was carried out as described in Example 1.

M_n : 9400; M_w : 24200; The glass transition temperature T_g was 133°C.

15 Example 5

- I. Conversion of THPE with octanoil chloride (molar ratio of 1:2)

20 1,2254 g of THPE (4 mmole) were brought into a 50 mL three-necked glass reactor and dissolved in 25 mL of dioxane. 1.2 mL of triethylamine were added and the solution was heated to 45°C. 1.3 g of octanoil chloride (1.368 mL, 8 mmole) were added at once and the solution was heated to 50°C. This temperature was kept for 3 hours. Ammonium chloride which was formed by the reaction and precipitated from the solution was separated by filtration.

- II. Polycondensation with bisphenol A and phosgene (2 mole percent of reaction product I based on bisphenol A)

25 A) Phosgenation: 4.468 g of bisphenol A were brought into a 100 mL reactor and dissolved in 23 mL of 1 n NaOH. 20 mL of methylene chloride were added. 6 ml of a triphosgene solution (4 g of triphosgene in 40 mL of dichloro methane) were slowly added (0.05 mL/10 seconds). The pH dropped to 12.3. 2.5 ml of the solution of the

reaction product, as prepared in paragraph I above in dioxane were added at once. The pH dropped to 11.7. Phosgenation was further continued by slowly adding 6 mL of the triphosgene solution. Then a solution of 0.122 g of p-tert-butylphenol in 4 mL of methylene chloride was added as a chain terminator. The molar ratio of bisphenol A to the chain terminator was 24.6:1. Phosgenation was continued by adding another 12 mL of the triphosgene solution. The pH was 8.8. Coupling of the oligomers was achieved by adding 2 mL of a triethylamine solution (2.5 g in 10 mL of methylene chloride) and 2 mL of 30 percent aqueous NaOH. The solution was allowed to stir for another 10 minutes.

III. Isolation and purification

The solution was brought into a phase separator. The aqueous phase was separated. The organic phase was washed with 50 mL of 2 N-HCl and subsequently 3 times with 75 mL of distilled water.

The organic phase was dried over Na_2SO_4 free of water, filtrated and the solution was evaporated. The polymer film obtained was dried in vacuum at 90°C.

M_n (g/mole): 8700; M_w (g/mole): 22800.

The polymer film was broken up in smaller pieces and pressed into a tablet of 1 cm diameter and 0.5 cm thickness. The rheology curve was measured by using a Physica OS 300, whereby the tablet was brought between a cover and a plate. The temperature was 280°C. The melt viscosity (Pa.s) was plotted versus the shear rate (frequency, Hz). The material was characterized by having a high flow and low zero shear viscosity.

The T_g was 112°C.

<u>Frequency (Hz)</u>	<u>Viscosity (Shear stress, Pa.s)</u>
0.2	93
1.6	110
3.75	69
8.6	75
20	76

For comparative purposes the melt viscosity of a polycarbonate is listed which was branched with 0.35 mole percent of THPE, but which did not contain groups of Formula II according to the present invention.

	<u>Frequency (Hz)</u>	<u>Viscosity (shear stress Pa.s)</u>
5	0.2	2880
	1.6	2380
	3.75	1960
	8.6	1500

10 Example 6

I. Conversion of THPE with octanoil chloride (molar ratio 1:1)

1,2254 g of THPE (4 mmole) were dissolved in 25 mL of dioxane and brought into a glass reactor. 0.6 mL of triethylamine were added and the reactor was heated to 45°C. 0.650 g (0.685 mL, 4 mmole) of octanoil chloride were added at once. The solution was heated to 50°C and kept at this temperature for 3 hours. The formed NH_4Cl was filtered off.

II. The polycondensation with bisphenol A and phosgene (2 mole percent reaction product I based on bisphenol A) and the addition of solution I was carried out under the same conditions (amount) as described in the previous Example 5.

M_n (g/mole): 9500; M_w (g/mole): 31000; T_g is 130 °C.

The rheology curve was measured as described in Example 5.

<u>Frequency (Hz)</u>	<u>Shear Stress (Pa.s)</u>
0.2	675
1.6	602
3.75	540
8.6	450
20	350

25

Example 7I. Conversion of THPE with 1-chlorotrimethyl-silane (molar ratio 1:1)

5 1,2254 g of THPE (4 mmole) were brought into a 100 mL reactor and were dissolved in 20 mL of dioxane. 0.6 mL of triethylamine were dissolved in 20 mL of 1,4-dioxane and added at room temperature within 30 minutes. 0.435 g of Cl-Si(CH₃)₃ were dissolved in 10 mL of dioxane and added to the solution within 10 minutes. Post reaction at 60°C for 2 hours.

10 II. Polycondensation with bisphenol A and phosgene

The polycondensation was carried out as described in Example 5, however, the reaction product I was added from the beginning to the monomer solution and a molar ratio of bisphenol to chain terminator of 44:1 was used. 4.68 g of bisphenol A
 15 dissolved in 23 mL of 1.5 n NaOH, 20 mL of dichloromethane and 5.0 mL of the reaction solution I above were used. Phosgenation was carried out as described in Example 5. After the addition of half of the total amount of the triphosgene solution in dichloromethane (12 mL), 4 mL of a solution of 0.425 g of p-tert-butylphenol in 25 mL of methylene chloride were added. Further phosgenation, coupling, purification and
 20 isolation of the polymer was carried out as described in Example 5.

The rheology curve was measured as described in Example 5.

M_n (g/mole): 9700; M_w (g/mole) 33700. T_g is 127°C.

25

<u>Frequency (Hz)</u>	<u>Shear Stress (Pa.s)</u>
0.2	745
1.6	533
3.75	320
20	160

The results of the previous examples are listed in the following Table:

Synthesis parameters

Characterization of the polymers

	TFM ¹⁾ (A)	Alkyl. Agent (B) ²⁾	Molar ratio (A) / (B)	T _g (°C)	Molar ratio bis A/PTBP ³⁾	M _n	M _w
1	TMTC	dodecanol	1:1	137	44:1	13 100	50 800
2	TMTC	polyoxy- ethylene-(4)- laurylether Brij 30, Aldrich	1:1	132	44:1	13 200	55 700
3	THPE	octyl bromide	1:1	129	44:1	13 600	34 700
4	1,3,5- trihydroxy- benzene	octanoil chloride	1:1	133	24.6:1	9 400	24 200
5	THPE	octanoil chloride	1:2	112	24.6:1	8 700	22 800
6	THPE	octanoil chloride	1:1	130	24.6:1	9 500	31 000
7	THPE	chlorotri- methyl silane	1:1	127	44:1	9 700	33 700
8	TMTC	dodecanol	1:1	134	24.6:1	9 800	29 100
9	THPE	octanoil chloride	1:1	132	44:1	12 700	46 500

5 ¹⁾ Trifunctional monomer

²⁾ Alkylating agent

³⁾ Bisphenol A/p-tert-butylphenol

Example 8

- 10 The polycarbonate was produced as described in Example 1, except that the molar ratio of bisphenol A to p-tert-butylphenol is 24.6.

Example 9

The polycarbonate was produced as described in Example 6, except that the molar ratio of bisphenol A to p-tert-butylphenol is 44.

- 15 Example 10

THPE was reacted with octanoil chloride as described in Example 5 except that the molar ratio of THPE to octanoil chloride was 1:1.5.

The product distribution of the reaction products between THPE and octanoyl chloride in Examples 5, 6 and 10 were determined by ^1H -NMR and ^{13}C -NMR and are listed in the following table:

Example	<u>6</u>	<u>10</u>	<u>5</u>
Molar ratio of THPE to octanoyl chloride	1:1	1:1.5	1:2
Reaction Products (mole %)			
THPE (non-reacted)	39.7	17.2	6.5
Monosubstituted THPE	31.5	35.1	23.4
Disubstituted THPE	21.9	30.9	36.4
Trisubstituted THPE	6.8	16.8	33.8

5

Example 11

I. Conversion of THPE with octanoyl chloride (molar ratio 1:2)

10 To a 500 mL one-neck round bottom flask were added 1,1,1-tris-(4-hydroxyphenyl)ethane (THPE, 20.0 g, 65.3 mmole) and dioxane (306 g). The mixture was stirred magnetically to dissolve the THPE. Triethylamine (14.5 g, 143.6 mmole) was added in one portion, followed by addition of octanoyl chloride (20.96 g, 128.8 mmole) via a syringe pump over 10 minutes. After addition was complete, the mixture was stirred for 5 minutes,

15 then it was poured into a separatory funnel. The mixture was washed with 1 N HCl (1 X 100 mL). Then 20 mL methylene chloride was added to clarify layers. The aqueous phase was separated and discarded. The organic phase was washed with water (1 x 100 mL); then 20 mL methylene chloride was added to clarify layers. The aqueous phase was separated and discarded. The organic phase was dried over MgSO_4 , filtered and then evaporated to give a

20 viscous yellow liquid. The obtained THPE (ester) mixture was analyzed by liquid chromatography and revealed a mole ratio of 4.0/28.3/35.5/32.2 THPE/mono-octyl ester/di-octyl ester/ tri-octyl ester. The chromatography was calibrated with pure THPE esters obtained by thin layer chromatography of a small portion of the reaction mixture.

II. Synthesis of Polycarbonate Using the Product Mixture Produced in I. above

To a two liter baffled resin kettle were added bisphenol-A (100 g, 438 mmole), p-tert-butylphenol (1.84 g, 12.3 mmole), the THPE (ester) mixture produced according to I. above (4.85 g, 8.76 mmole), water (692 g) and methylene chloride (500 g). Nitrogen was
5 purged through the system for 15 minutes, then 50 percent NaOH (82 g, 1029 mmole) was added and the mixture was stirred to dissolve the monomer. Phosgene gas (55 g, 556 mmole) was bubbled in over 45 minutes followed by more 50 percent NaOH (27 g, 338 mmole), and triethylamine (8.17 g of 5 percent in water, 4 mmole). Chloroformates were consumed within 10 minutes. The reaction phases separated slowly, then the aqueous
10 phase was separated and discarded. The organic phase was washed with 1 weight percent concentrated HCl, followed immediately by 10 weight percent water. The aqueous phase was removed and discarded. The organic phase was washed 3 more times with 10 weight percent water. Then the methylene chloride was removed by dropping the polycarbonate solution into boiling water. The collected polymer had an Mw of 34,960 and an Mn of
15 11,190. The T_g was 137°C.

Example 12

Example 11 was repeated, however a THPE (ester) mixture containing THPE/mono-octyl ester/di-octyl ester/ tri-octyl ester at a mole ratio of 10.2/55/26.5/8.3 was used for the production of the polycarbonate instead of the product mixture obtained
20 according to Example 11.1 above. The produced polymer had an Mw of 48,560 and an Mn of 19,910. The T_g was 144°C.

Example 13

THPE was reacted with octanoyl chloride at a molar ratio of 1:2 as described in Example 11.1 above.

25 To a 100 mL narrow mouth jar were added bisphenol-A (5 g, 22 mmole), p-tert-butylphenol (0.134 g, 0.89 mmole), the THPE (ester) mixture obtained according to Example 11.1 above (0.2428 g, 0.44 mmole) and water (35 g). Fifty percent NaOH (3.68 g, 46 mmole) was added and the mixture stirred magnetically to dissolve the monomer. A phosgene solution (35.6 g of a 8.5 percent solution in methylene chloride, 30.7 mmole) was
30 added in one portion by syringe over 5 seconds followed by shaking for 30 seconds. More than 50 percent NaOH (2.63 g, 32.9 mmole) was added in one portion followed by shaking

for 30 seconds. Finally, triethylamine (0.41 g of 5 percent in water) was added and chloroformates were consumed within 3 minutes. The phases separated slowly, then the aqueous phase was separated and discarded, followed by washing the organic phase with 1 N HCl (1 X 20 mL) and water (2 X 20 mL). The methylene chloride was evaporated on a hot plate to give a film having a T_g of 138°C, and $M_w = 24730$, $M_n = 12470$.

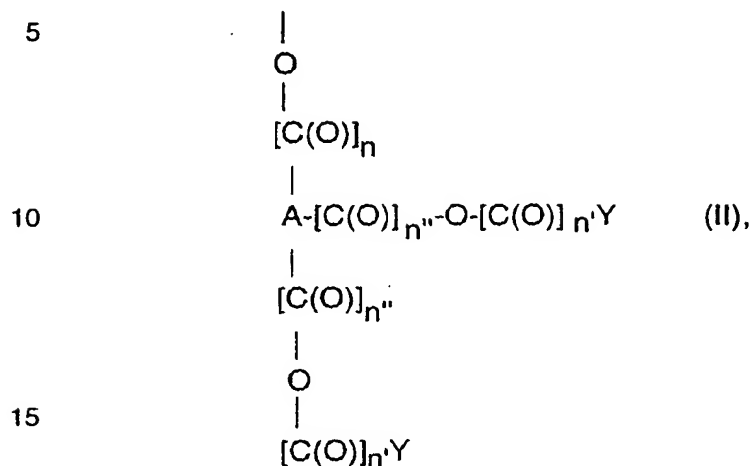
Examples 14-18

Example 13 was repeated, however the molar ratio of p-tert-butylphenol (PTBP)/bisphenol A (Bis-A) and/or the molar ratio of THPE (ester) mixture/Bis-A was varied. The corresponding ratios and results in Examples 13-18 are listed below

10	<u>Ex.</u>	<u>PTBP/Bis-A</u>	<u>THPE (Esters)/Bis-A</u>	<u>T_g°C</u>	<u>M_w</u>
	13	0.041	0.02	138	24730
	14	0.041	0.05	124	25970
	15	0.041	0.10	106	26540
	16	0.028	0.02	142	35540
15	17	0.028	0.05	125	33690
	18	0.028	0.10	107	33690

Claims:

1. A polycarbonate containing an end-capping group of Formula II



wherein

A is an aliphatic hydrocarbon group or a group containing 1 or 3 aromatic or heteroaromatic rings to which the oxygens or carboxyl groups are directly linked, with the proviso that A does not contain a heteroatom outside the aromatic ring(s),

n is 0 or 1,

n' is 0 or 1, n'' is 0 or 1, provided that n' is 0 when n'' is 1,

Y is a hydrocarbon group or

a group of Formula $-(\text{CH}-)_m[\text{E}-(\text{CH}-)_m]_p-(\text{alkylene})_q-\text{H}$ (VI),



wherein

E in each occurrence independently is O, R₂Si or R₂Si-O,

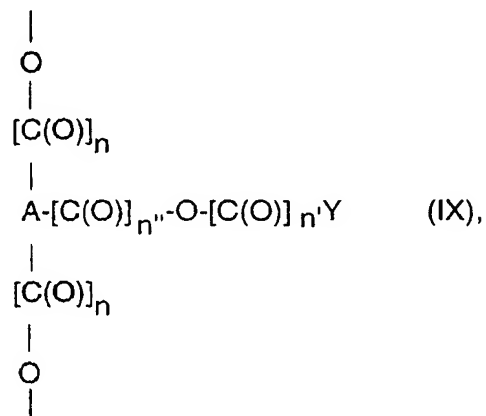
R in each occurrence independently is H or C₁₋₆-alkyl,

m in each occurrence independently is 0, 1, 2, 3, or 4,

p is from 1 to 50 and

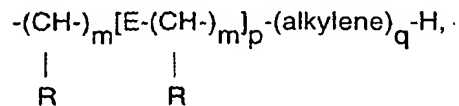
q is 0 or 1.

2. The polycarbonate of Claim 1 containing additionally one or more groups of Formula IX copolymerized in the polymer backbone,



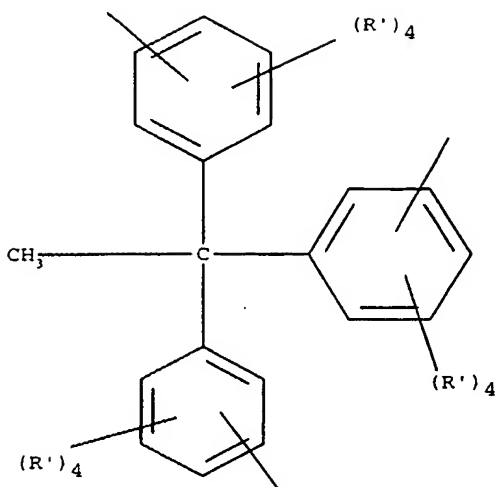
wherein A, Y, n, n' and n'' have the meanings indicated in Claim 1.

3. The polycarbonate of Claim 1 or Claim 2 wherein in the group of Formula II and/or IX Y is alkyl or a group of Formula



wherein E, R, m, p and q have the meanings indicated in Claim 1.

4. The polycarbonate of any one of Claims 1 to 3 wherein, in the group of Formula II and/or Formula IX, A is



n is 0, n'' is 0,

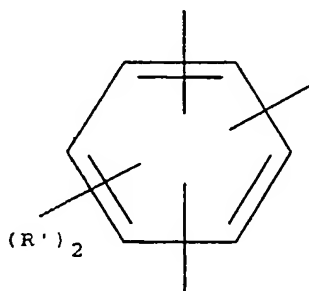
n' is 0 or 1,

R' in each occurrence independently is hydrogen, alkyl or alkoxy, and

5

Y has the meaning indicated in Claim 1 or Claim 3.

5. The polycarbonate of any one of Claims 1 to 3 wherein, in the group of Formula II and/or Formula IX, A is



10

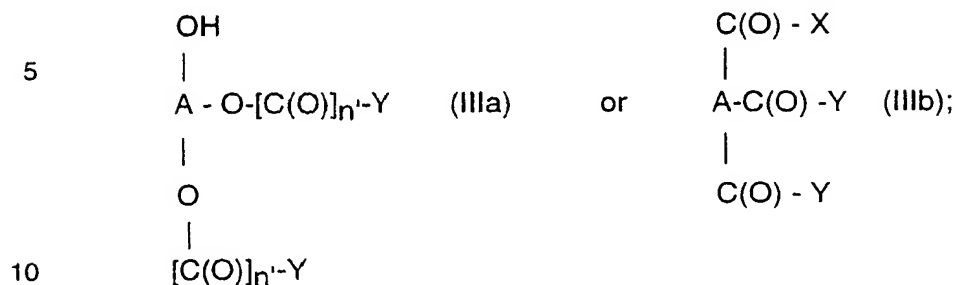
n is 0 or 1, n'' is 0 or 1,

R' in each occurrence independently is hydrogen, alkyl or alkoxy, and

Y and n' have the meanings indicated in Claim 1 or Claim 3.

6. The polycarbonate of any one of Claims 1 to 5 being a reaction product of
at least

- (1) a carbonate precursor,
 (2) a dihydric phenol and
 (3) a compound of Formula IIIa or IIIb



wherein

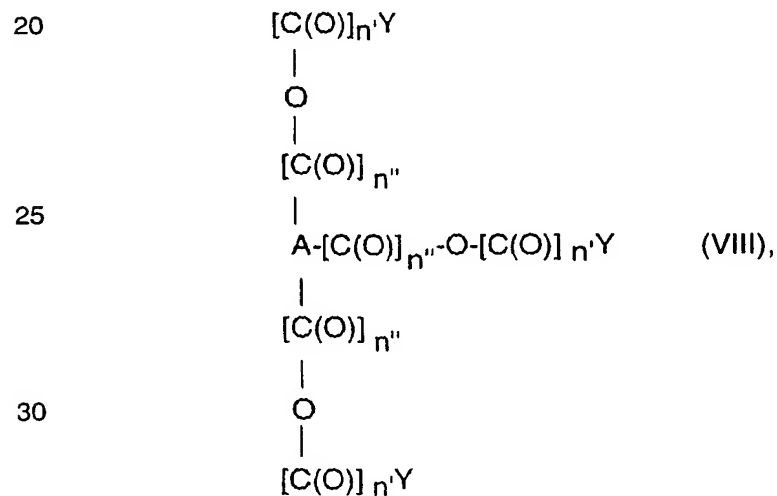
X is halogen,

n' is 0 or 1,

15 and A and Y have the meanings indicated in Claim 1, 3, 4 or 5.

7. The polycarbonate of Claim 6 wherein the molar ratio between the compound of Formula IIIa or IIIb and the dihydric phenol is from 0.0001:1 to 0.25:1.

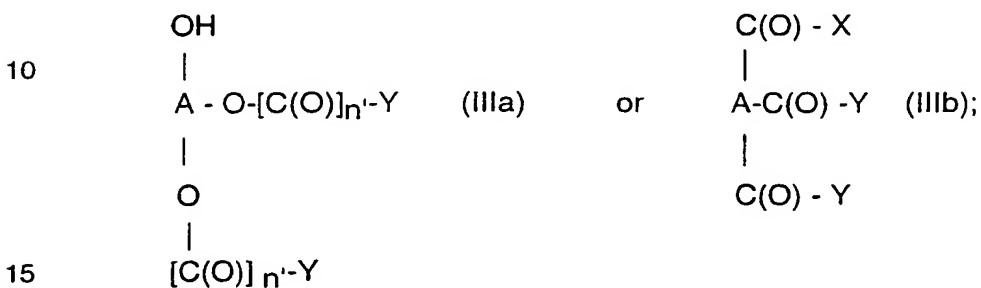
8. A polycarbonate composition containing the polycarbonate of any one of Claims 1 to 7 and a compound of Formula VIII



wherein A, Y, n' and n'' have the meanings indicated in Claim 1, 3, 4 or 5.

9. A process for producing the polycarbonate of any one of Claims 1 to 7 which comprises reacting at least

- 5 (1) a carbonate precursor,
 (2) a dihydric phenol and
 (3) a compound of Formula IIIa or IIIb



wherein

X is halogen,

n' is 0 or 1,

and A and Y have the meanings indicated in Claim 1, 3, 4 or 5.

20 10. The process of Claim 9 wherein the compound of Formula IIIa is produced *in situ* by reacting a compound of Formula IVa

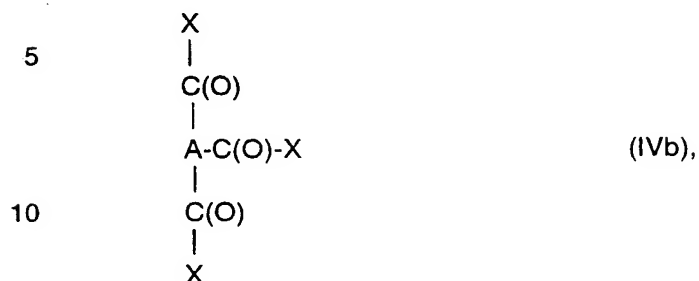


with a compound of Formula Va



wherein A and Y have the meanings indicated in Claim 1, 3, 4 or 5 and X' is halogen, -C(O)-halogen, -C(O)OH or epoxy.

11. The process of Claim 9 wherein the compound of Formula IIIb is produced *in situ* by reacting a compound of Formula IVb



with a compound of Formula HO-Y,

15 wherein X is halogen and A and Y have the meanings indicated in Claim 1, 3, 4 or 5.

12. A molded article produced from the polycarbonate or polycarbonate composition of any one of Claims 1 to 8.

13. The molded article of Claim 12 produced by blow-molding.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/21698

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G64/14 C08G64/16 C08G64/06 C08K5/103 C08K5/107
C08K5/12 C08K5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C07C C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 20 64 095 A (BAYER AG) 6 July 1972 see claims 1-6	8, 12
A	EP 0 230 608 A (GENERAL ELECTRIC COMPANY) 5 August 1987 cited in the application see page 2, line 11 - line 17; claims 1-4	1-3, 5-7, 9, 12, 13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/21698

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